Electron spin resonance and optical spectral studies of a titanium(III) complex formed with nitrilotriacetic acid

P. I. PREMOVIĆ and LY S. JOVANOVIĆ

Laboratory of Geochemistry, Department of Chemistry, Faculty of Science,
University of Niš, YU-18000 Niš

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On adding more than two moles of nitrilotriacetic acid (NTA) to a solution of Ti(III) at pH 4 to 10 containing 10—20 M tartaric acid, a solution is obtained that exhibits a rather sharp ESR absorption signal ($g_0 = 1.963 \pm 0.001$, the linewidth $\Delta H_{\text{p—p}} = (0.30 \pm 0.05)$ mT). A constant maximum signal level is observed under basic conditions: pH 4 to 10. Measurement of the integrated intensity of the maximum signal indicated that (90 ± 10) % of Ti(III) is in the complex. The variation and mole ratio methods based on the measurement of the ESR signal and optical absorption maximum (at $\tilde{\nu} = 14\,000\ \text{cm}^{-1}$), respectively, for determining the composition of this complex ion indicate that the concentration ratio Ti(III) to NTA is 1 : 2. The experimental **g**-tensor components ($g_x = 1.946 \pm 0.001$, $g_y = 1.959 \pm 0.001$, and $g_z = 1.997 \pm 0.001$) derived from the frozen solution ESR spectrum of this Ti(NTA)_2 paramagnetic species are consistent with an axially elongated octahedral structure with an equatorial rhombic distortion through bidentate NTA ligands. Significant in-plane σ and π bonding is indicated in this octahedron of the $\mathbf{D}_{2h}$ symmetry. It is proposed that there is at least one axial hydroxide ligand.

The use of sodium nitrilotriacetate (Na_3NTA) as a detergent builder in some countries [1, 2] and the subsequent detection of the ligand in the environment [3] have stimulated interest in its chemistry. As a rather strong chelating agent NTA forms complexes with heavy metals present in water modifying their toxicity toward aquatic life [4, 5] and their mobility in the environment [6—9].

Using ESR and optical spectroscopy *Fujiwara et al.* [10—12] carried out a survey of the complexation of Ti(III) ions with nitrogen containing organic chelating agents in aqueous solutions. Among these reagents (EDTA, amino acids and related compounds) they found out that NTA forms the most stable complex.

Their descriptive ESR study can be summarized as follows:

a) A 0.1 M-Ti(III) solution containing 0.1 M-NTA shows no ESR signal in strongly acid solution (pH ≤ 1.5);

b) A signal appears at pH 1.7 increasing to a maximum at pH 4 and remaining constant to pH 10. No ESR signal intensity measurements were given.

Fujiwara and coworkers [10, 11] also reported on optical studies, though failing to relate trends in the spectra explicitly to the ESR data either in pH variation or intensity. A complex at pH 1 (not ESR active) yielded a blue solution with maximum absorbance at $\tilde{\nu} = 15\,500\ \text{cm}^{-1}$ At pH 4.7 a greenish--yellow solution is observed that exhibited maximum absorbance at $\tilde{\nu} = 14\,000\ \text{cm}^{-1}$

They established that the blue complex, predominant at pH 1.5, has stoichiometry 1 1, and that the greenish-yellow complex, predominant at pH 4—10, has stoichiometry 1 : 2. Later *Watanable* and *Fujiwara* [12] studied ESR spectra of 15 kinds of Ti(III) chelates in aqueous solutions at room temperature including NTA. The nature of chemical bonding in these Ti(III) chelates was discussed with the interpretation of the *g*-factors, hyperfine coupling constants and the maximum absorption wavelength in the visible absorption spectra on the basis of a simple crystal field (CF) theory. Assuming that the local point symmetry of Ti(III) complex ions in the chelate complexes in aqueous solution was a tetragonally compressed octahedron ($\mathbf{D}_{4h}$ symmetry), they found that covalency played a significant role in these complexes. The ESR relaxation mechanism was also studied and it was suggested that the Orbach process, equivalent to the vibrational spin-orbit mechanism through spin-orbit coupling, was the predominant one.

In examining the reports of these workers one is struck by the lack of correlation between optical and ESR measurements and the failure to determine the structure of the complex involved or even the local point symmetry. Indeed, our preliminary qualitative examinations of the Ti(III)—NTA system showed several novel observations. Bearing in mind the relative practical importance of Ti—NTA system it seemed timely to reinvestigate this system.

Experimental

All spectra were recorded on a Varian E-65 X-band ESR spectrometer operating at 100 kHz modulation. Frozen solution samples were contained in cylindrical quartz cells (5 mm o.d.). Solution spectra at room temperature were recorded in standard Varian E-248 flat cells.

The variable temperature measurements employed an apparatus based on the Varian V-4520 approach constructed from dewar components supplied by Scanco Quartz (California). A controller similar to the Varian V-6040 was modified to use an Rdf. Corp. platinum-platinum resistance sensor (EP-110, 100 Ω). The calibration was achieved using a Hewlett-Packard 2802 A thermometer. Samples maintained at (210 ± 3) K ($CHCl_3$—CO_2 slush bath) or at (197.5 ± 3) K (powdered dry ice) were continuously monitored by the digital thermometer probe with the sample adjacent in the coolant.

The *g*-factors are quoted relative to 2,2-di(4-*tert*-octylphenyl)-1-picrylhydrazyl (DPPH, Aldrich) using a solid sample (linewidth $\Delta H_{p-p} = (0.10 \pm 0.01)$ mT, $g = 2.0036 \pm 0.0002$) that was permanently maintained in a dual cavity assembly (Varian E-232). The field shift between the two cavities had been carefully measured. DPPH powder, to be used as a primary standard in determining *g*-factors, was prepared by drying at *ca.* 340 K for 4—5 h. A weighed and powdered amount of DPPH reagent was used as received. Hyperfine splitting constants were determined relative to a solution of potassium nitrosodisulfonate (Fremy's salt) for which $g = 2.0055 \pm 0.0001$ and the nitrogen splitting constant $a_N = (1.309 \pm 0.001)$ mT [13].

Spin concentration of Ti(III) ions in the samples was determined by the sample interchange method [14]. The solution of a metal salt that was used as a primary standard in determining spin concentrations was prepared as follows. A weighed amount of the salt (Fisher reagent grade, used as received) was dissolved in bidistilled water that had been purged with nitrogen to remove dissolved carbon dioxide and oxygen. Solutions of copper(II) nitrate, chromium(III) nitrate, manganese(II) sulfate, and vanadium(IV) oxide sulfate were used in preparing standard samples of $[Cu(H_2O)_6]^{2+}$, $[Cr(NH_3)_6]^{3+}$, $[Mn(H_2O)_6]^{3+}$, and $[VO(H_2O)_5]^{2+}$ All concentration results were confirmed both by two or more experiments on different days and the use of more than one reference compound in each case. Further details of the measuring procedure and associated controls for precision and accuracy are given in paper [15].

Frozen solutions measured only at 77 K were obtained by rapidly quenching the sample in liquid nitrogen, maintaining the sample in the Varian E-246 insert dewar. Details of temperature variation experiments are included with the results.

Ultraviolet (UV) and visible (VIS) absorption spectra were recorded at room temperature on a Cary Model 17 instrument using 1 cm or 1 mm quartz cells.

Preparation of Ti(III) *solutions and complexes*

Ti(III) solutions were prepared by dissolving the metallic sponge (Fisher) with gentle heating in approximately 1—2 M hydrochloric or sulfuric acid. An N_2 atmosphere was employed to minimize oxidation of Ti(III) ion. Alternatively, Fisher reagent Ti(III) chloride solution (20%) or commercial BDH reagent Ti(III) sulfate solution (15%) were used directly without qualitative change in any of the results reported in this paper. The final concentration of Ti(III) ions was determined volumetrically by titration with a ceric sulfate solution using *o*-phenanthroline as indicator. Typical values obtained for either stock solutions or solutions prepared by dissolving the metal lay in the range 95—97%. The chelating reagents used in this work, NTA and tartaric acid (TA), were both reagent grade Eastman chemicals used as received.

All pH measurements were made to within ±0.1 units using an Acumet pH-meter equipped with a combination electrode. Final pH adjustment was made by addition of either the appropriate diluted acid or sodium hydroxide.

Results and discussion

ESR observations

On adding slightly more than two equivalent amounts of NTA to 0.02 M-Ti(III) ions from either the chloride or the sulfate in a yellow solution containing 10—20 M-TA at pH 4 to 10, a greenish-yellow solution was obtained that exhibited a rather sharp ESR absorption signal (Fig. 1). Spectral parameters for this complex are given in this figure. At higher gain, the satellites lines from ^{47}Ti and ^{49}Ti interactions were evident.

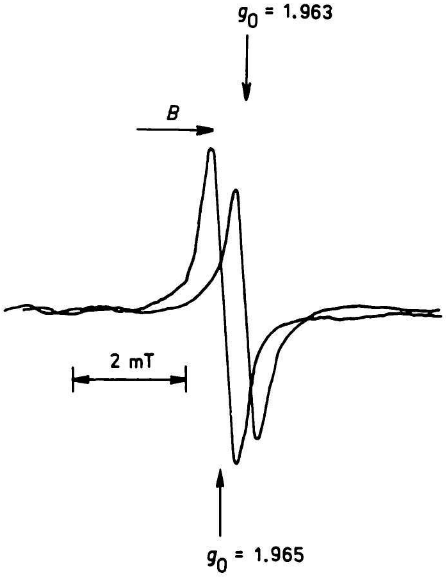


Fig. 1. ESR spectra of the Ti(III)—NTA system: 0.01 M-TiCl$_3$, the ratio [Ti^{3+}]:[NTA] = = 1 : 20, pH 7.5 and 2.1.

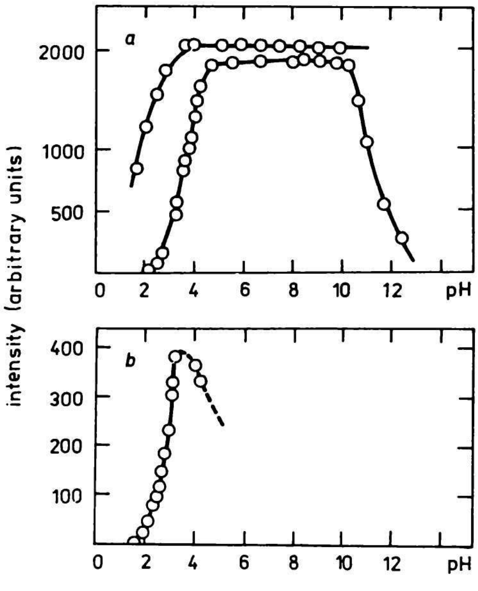


Fig. 2. a) The pH dependence of proposed Ti(NTA)$_2$ complex ion. Upper curve: absorbance at $\tilde{\nu}$ = 14000 cm^{-1}, lower curve: ESR signal intensity. 0.02 M-TiCl$_3$, [Ti^{3+}] [NTA] = 1:20.
b) The pH dependence of the second ESR signal. 0.02 M-TiCl$_3$, [Ti^{3+}]:[NTA] = = 1:20.

The pH dependence of the intensity of the ESR signal is shown in Fig. 2*a* for a solution derived from 0.02 M-TiCl$_3$ and with the ratio [Ti^{3+}]:[NTA] = 1 : 20. A constant maximum signal level is observed under basic conditions (pH 4 to 10). Outside this range the signal steadily decreases until it is no longer observable at *ca.* pH 13 and 1.9. Measurement of the integrated intensity of the maximum signal indicated that (90 ± 10)% of the Ti(III) was in the complex.

Fig. 3 shows the variation method for determining the composition of this paramagnetic species based on the ESR signal. Fig. 4 shows the mole ratio method for establishing the concentration ratio of Ti^{3+} to NTA in the same species. The ratio is clearly shown to be 1 to 2 by both procedures. These studies of the ESR signal intensity (Figs. 3 and 4) combined with approximate absolute concentration measurement demonstrated that $[Ti^{3+}]:[NTA] = 1:2$ paramagnetic species was one of the most stable complexes in solution in the pH range 4 to 10.

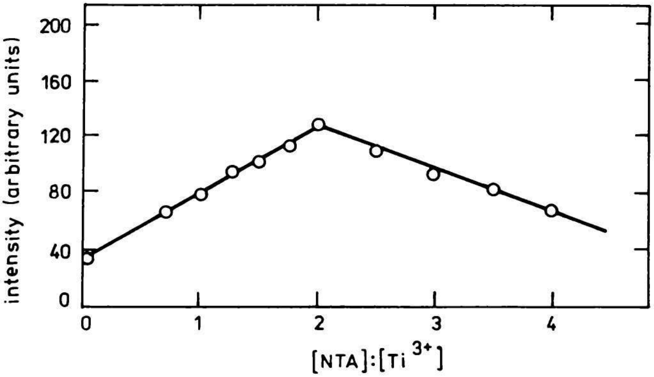


Fig. 3. Establishment of the ratio [Ti(III)] to [NTA] at pH 9.1, 0.01 M-$TiCl_3$, by the continuous variation method, ESR signal.

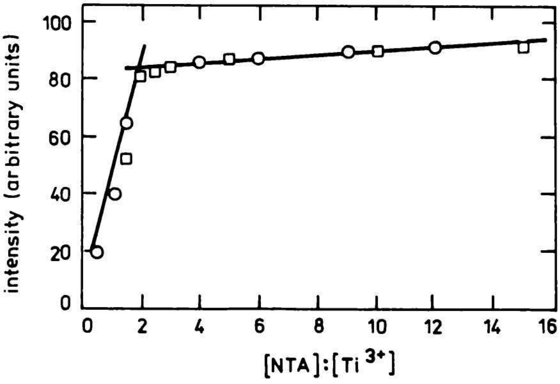


Fig. 4. Establishment of the ratio [Ti(III)] to [NTA] at pH 9.1, 0.01 M-$TiCl_3$, by the mole ratio method, the absorption maximum at $\tilde{\nu} = 16700\ cm^{-1}$.

Note that such preparations are carried out in the presence of excess TA. Experimentally hydrolysis of the Ti(III) ions is prevented by TA (presumably a kinetic competition phenomenon); though the eventual complex formed does not contain TA ion. Preparations omitting this reagent though partially hydrolyzed show the same optical and ESR spectrum. Moreover varying the concentration of TA had no measurable effect on the ESR signal intensity at

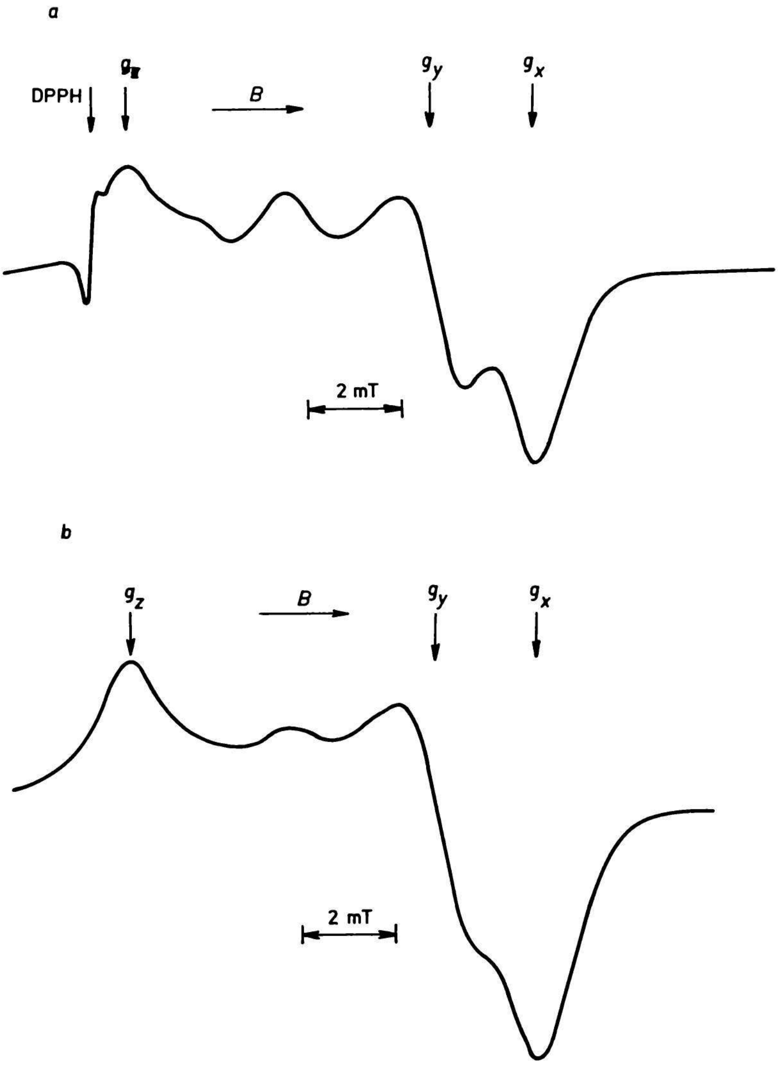


Fig. 5. ESR spectra of the system: 0.01 M-TiCl$_3$, [Ti^{3+}]:[NTA] = 1:80, frozen solution. *a*) pH 7.5; *b*) pH 3.0. $g_x = 1.946 \pm 0.001$, $g_y = 1.959 \pm 0.001$, and $g_z = 1.997 \pm 0.001$.

room temperature or on the frozen solution spectrum (see below). Such control experiments were not reported by *Fujiwara et al.* [10—12].

In the pH range 1.0—3.5 the aqueous solution of the complex derived from chloride and sulfate of Ti(III) exhibited a rather sharp new ESR signal (Fig. 1) with the experimental room temperature value $g_0 = 1.965$. At higher gain the satellite lines from ^{47,49}Ti interaction were also observed with $|a_{\mathrm{Ti}}| = (1.50 \pm 0.02)$ mT. Measurements of the integrated intensity of the maximum signal indicated that ≈ 5% of the Ti(III) was in this complex. Notice that at the higher pH values both signals are clearly evident.

The pH dependence of the second ESR absorption signal is shown in Fig. 2*b*, for 0.02 M solution. From a maximum level at pH ≈ 3.5 the signal intensity diminished until it was no longer observable at pH 1.0.

The spectrum of a frozen aqueous solution of $[\mathrm{Ti}^{3+}]:[\mathrm{NTA}] = 1$ 80 at pH 7.5 is shown in Fig. 5*a*. The values of g_x, g_y, and g_z principal components of the **g**-tensor are assigned on the basis of theoretical consideration carried out by *Kneubühl* [16] for a randomly oriented sample with the paramagnetic unit having a nonaxial **g**-tensor. The calculated isotropic g_0-factor is found to be in reasonable agreement with the experimental room temperature value $g_0 = 1.963 \pm 0.001$. The presence of another paramagnetic species in low content in frozen solution spectra is evident (see Fig. 5*a* and compare with Fig. 5*b*).

Optical observations

In the pH range 4—10 the greenish-yellow aqueous solution of the complex derived from $\mathrm{TiCl_3}$ or $\mathrm{Ti_2(SO_4)_3}$ exhibited the same optical spectrum in the presence of excess NTA, with a relatively broad absorption maximum at $\tilde{\nu} = 14\,000\ \mathrm{cm^{-1}}$ ($\{\varepsilon\} \approx 6$) and a relatively sharp band at $\tilde{\nu} \approx 50\,000\ \mathrm{cm^{-1}}$ ($\{\varepsilon\} > 1000$). The pH dependence of the absorbance at $\tilde{\nu} = 14\,000\ \mathrm{cm^{-1}}$ in the pH range 1.9 to 10.0 is given in Fig. 2*a*. The decay of this absorbance does not follow the decay of the ESR signal indicating that a species showing no ESR signal is formed from the ESR active "$\mathrm{Ti(NTA)_2}$" complex ion at $2 \leq \mathrm{pH} \leq 4$. However, these species must show approximately the same optical spectra. Below pH 1.9 interference from a relatively high concentration of the blue complex "$\mathrm{Ti(NTA)_1}$" made the pH dependence of the absorbance at $\tilde{\nu} = 14\,000\ \mathrm{cm^{-1}}$ unreliable.

In Fig. 6 the variation method is applied to the optical spectrum establishing the $[\mathrm{Ti}^{3+}]:[\mathrm{NTA}]$ ratio of the complex present at pH 3. The ratio is clearly shown to be 1 to 2 by this procedure. Finally, Fig. 7 shows the mole ratio method utilizing the maximum absorption at $\tilde{\nu} = 16\,700\ \mathrm{cm^{-1}}$ (blue solution) applied at pH 1.5. The ratio is clearly shown to be 1 1 by this procedure. The increase (between pH 2.1 to 1.5) and the decay (between pH 1.5 to 1.0) of the absorbance at $\tilde{\nu} = 16\,700\ \text{cm}^{-1}$ was smoothly followed by the increase and the decay of absorbance at $\tilde{\nu} = 41\,000\ \text{cm}^{-1}$ ($\{\varepsilon\} \approx 800$). Such an observation immediately suggests that a charge-transfer absorption band at $\tilde{\nu} = 41\,000\ \text{cm}^{-1}$ results from a charge-transfer electronic transition in the "Ti(NTA)$_2$" complex ion, probably involving the carboxylate ligand.

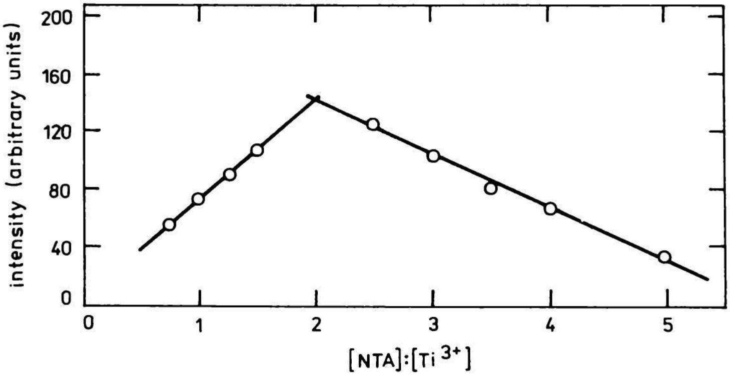


Fig. 6. Establishment of the ratio [Ti(III)] to [NTA] at pH 3.0, 0.01 M-TiCl$_3$, by the method of continuous variation, the absorption maximum at $\tilde{\nu} = 14\,000\ \text{cm}^{-1}$

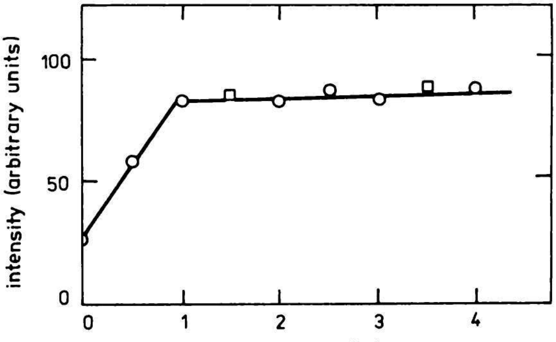


Fig. 7. Establishment of the ratio [Ti(III)] to [NTA] at pH 1.5, 0.01 M-TiCl$_3$, by the mole ratio method, ESR signal.

In general, the optical data reported here for the "Ti(NTA)$_1$" and "Ti(NTA)$_2$" complex ions are in good agreement with the conclusions of *Fujiwara* and *Codell* [10].

Structure assignment

Although the composition of the Ti(III)—NTA complex providing at pH 4—10 ESR signal now seems firmly established as $[Ti^{3+}]:[NTA] = 1:2$, the questions of the local point symmetry and discrete complex structure are rather involved. If we adopt the approach that each NTA molecule is uniformly tridentate then $\mathbf{D}_{3d}$ symmetry can be predicted providing that the ligand field is determined only by the six oxygen atoms of the NTA ligand. On the other hand, the prediction of a discrete axis involving coordination by two other groups (Fig. 8) leads to an approximately octahedral arrangement with a small equatorial rhombic distortion $\mathbf{D}_{2h}$ symmetry providing that the ligand field is determined primarily by the six oxygen ligand donor atoms.

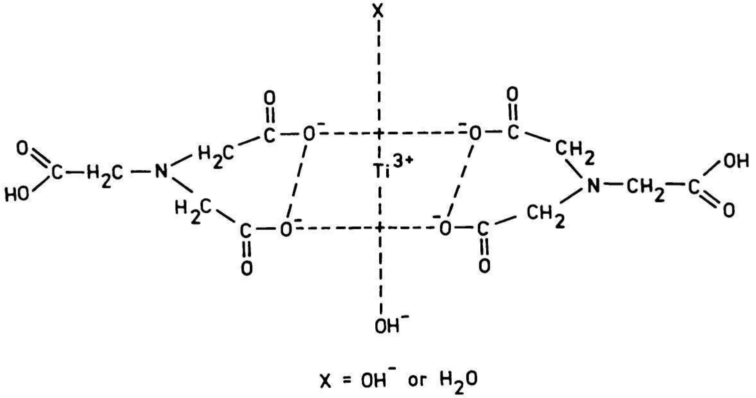

X = OH⁻ or H₂O

Fig. 8. Model of Ti(III) coordination in *trans*-$[Ti(NTA)_2X_2]$.

With $g_\perp \approx 1/2(g_x + g_y) = 1.953$ and $g_\parallel \approx g_z = 1.997$ we can propose that the ESR active "$Ti(NTA)_2$" complex ion has symmetry $\mathbf{D}_{3d}$ neglecting a small equatorial rhombic distortion. This assumption can be made since the actual difference between g_x and g_y is relatively small ($g_y - g_x = 0.013$). It should be noted that this structural model has already been proposed by *Fujiwara* and *Codell* [10].

In the $\mathbf{D}_{3d}$ symmetry the five orbitals are split into three energy states, one belonging to the A_{1g} representation and the other two to the E_g representation [17—19]. If we are dealing with $\mathbf{D}_{3d}$ symmetry then our experimental g-values are only consistent with A_{1g} as the ground state (Fig. 9) (if E_gA were ground state both $g_\parallel$ and $g_\perp$ are predicted to be close to zero) [19].

By analogy with the $[Ti(H_2O)_6]^{3+}$ complex ion [17—19] considering A_{1g} as the ground state we have

$$g_\parallel = 2.0023$$

$$g_\perp = 2.0023 - \frac{2\lambda_M}{\Delta E(A_{1g} \rightarrow E_g\mathrm{A})}\Phi^{\mathrm{A}} - \frac{4\lambda_M}{\Delta E(A_{1g} \rightarrow E_g\mathrm{B})}\Phi^{\mathrm{B}}$$

with the energy differences $\Delta E(A_{1g} \rightarrow E_g\mathrm{A, B})$ where λ_M (154 cm^{-1}) is the Ti spin-orbit coupling constant and $\Phi^{A,B}$ is a complex function employed to estimate covalency. The magnitude of $\Phi^{A,B}$ is mainly determined by the appropriate molecular orbital coefficients. However, the value of $\Phi^{A,B}$ lies between 0 and 1 tending to unity as the σ and π bonding becomes more ionic, and conversely [19]. Assuming that we are dealing with a nearly purely ionic case, *i.e.* $\Phi^{A,B} \rightarrow 1$ we can easily calculate from the $g_\perp$ expression, $g_\perp \approx 1/2(g_x + g_y) = 1.953$, that $\Delta E(A_{1g} \rightarrow E_g\mathrm{A}) \approx 62\,000$ cm^{-1} Since we would expect the energy ΔE of the $A_{1g} \rightarrow E_g\mathrm{A}$ electronic transition to be *ca.* 3000 to 6000 cm^{-1} [19] we must anticipate unrealistically high covalency (*e.g.* $\Phi^{A,B}$ 0.05 to 0.1) to accommodate this possibility.

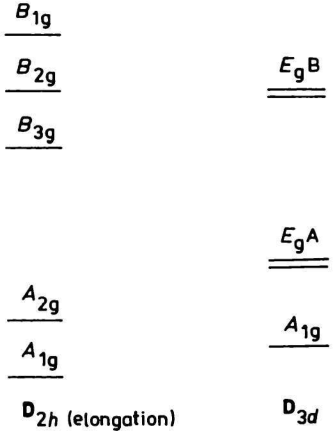


Fig. 9. Splitting of the ^2D term in ligand field of the $\mathbf{D}_{2h}$ (elongation) and $\mathbf{D}_{3d}$ symmetries.

On the basis of the above consideration we tentatively reject $\mathbf{D}_{3d}$ as the local point symmetry. The $3d^1$ in an octahedral ligand field with a small rhombic distortion ($\mathbf{D}_{2h}$ symmetry) has five energy states, B_{1g}, B_{2g}, B_{3g} and two A_g states (Fig. 9). Now the ESR spectrum cannot exhibit true axial symmetry. The difference between g_x and g_y arises from the difference in energy between the B_{2g} and B_{3g} states [18].

There are two possible cases of $\mathbf{D}_{2h}$ symmetry: *a*) compression, or *b*) elongation along the principal symmetry axis of the complex unit considered.

In the first case the corresponding expression for the g_z-component of the **g**-tensor is [18]

$$g_z = 2.0023 - \frac{8\lambda_M}{\Delta E(^2B_{1g} \rightarrow {}^2A_g)}\,\Phi_z$$

On the basis of this expression and assuming a purely ionic case ($\Phi_z \rightarrow 1$) one calculates that $\Delta E(B_{1g} \rightarrow A_g) = 246\,400$ cm^{-1} Since only the absorption band at

$\tilde{\nu} = 14\,000\ \mathrm{cm}^{-1}$ may correspond to the $B_{1g} \rightarrow A_g$ electronic transition we must anticipate again an unrealistically high covalency, *e.g.* $\Phi_z = 0.06$ to accommodate this possibility.

In the $\mathbf{D}_{2h}$ elongation symmetry both the metal orbitals $d_{x^2-y^2}$ and d_{z^2} belong to the A_g representation. Therefore the two a_g orbitals can be expressed as appropriate combinations of these.

Assuming that the ligands participate in bonding with s, p_x, p_y, p_z orbitals, the relevant antibonding MO's in terms of σ and π bonds are

$$a^*_{1g} = \alpha_1 d_{z^2} - m_1 d_{x^2-y^2} - \frac{1}{\sqrt{2}}\alpha'_1(\sigma^1_x - \sigma^3_x) - \frac{1}{\sqrt{2}}\alpha''_1(\sigma^2_y - \sigma^4_y) - \\ - \frac{1}{\sqrt{2}}\alpha'''_1(\sigma^5_z - \sigma^6_z)$$

$$a^*_{2g} = \alpha_2 d_{x^2-y^2} + m_2 d_{z^2} - \frac{1}{\sqrt{2}}\alpha'_2(\sigma^1_x - \sigma^3_x) - \frac{1}{\sqrt{2}}\alpha''_2(\sigma^2_x - \sigma^4_y)$$

$$b^*_{1g} = \beta_1 d_{xy} - \frac{1}{\sqrt{2}}\beta'_1(p^1_y - p^3_y) - \frac{1}{\sqrt{2}}\beta''_1(p^2_x - p^4_x)$$

$$b^*_{2g} = \beta_2 d_{xz} - \frac{1}{\sqrt{2}}\beta'_2(p^1_z - p^3_z) - \frac{1}{\sqrt{2}}\beta''_2(p^5_x - p^6_x)$$

$$b^*_{3g} = \beta_3 d_{yz} - \frac{1}{\sqrt{2}}\beta'_3(p^2_z - p^4_z) - \frac{1}{\sqrt{2}}\beta''_3(p^5_y - p^6_y)$$

The ligand donor atoms are placed in the same manner as in Fig. 10. In the above states σ^i are hybrid orbitals. The spin-Hamiltonian for Ti(III) in an octahedral ligand field with an equatorial rhombic distortion is

$$\hat{H} = \beta_e g_z H_z \hat{S}_z + \beta_e(g_x H_x \hat{S}_x + g_y H_y \hat{S}_y) + A\hat{S}_z\hat{I}_z + B_x\hat{S}_x\hat{I}_x + B_y\hat{S}_y\hat{I}_y$$

where

$$g_z = 2.0023 - \frac{8\lambda_\mathrm{M}}{\Delta E(A_g \rightarrow B_{1g})}\, m_z$$

$$g_x \approx 2.0023 - \frac{6\lambda_\mathrm{M}}{\Delta E(A_g \rightarrow B_{3g})}\,\Phi_x - \frac{2\lambda_\mathrm{M}}{\Delta E(A_g \rightarrow B_{3g})}\, m_x$$

$$g_y \approx 2.0023 - \frac{6\lambda_\mathrm{M}}{\Delta E(A_g \rightarrow B_{2g})}\,\Phi_y - \frac{2\lambda_\mathrm{M}}{\Delta E(A_g \rightarrow B_{2g})}\, m_y$$

$$A \approx P\left[\alpha_1^2\left(\frac{4}{7} - K_0\right) - m_1^2\left(\frac{4}{7} + K_0\right) - \frac{1}{7}(g_z - 2.00)\right]$$

$$B_x \approx P\left[-\alpha_1^2\left(\frac{2}{7}+K_0\right)+m_1^2\left(\frac{2}{7}-K_0\right)+\frac{15}{14}(g_x-2.00)\right]$$

$$B_y \approx P\left[-\alpha_1^2\left(\frac{2}{7}+K_0\right)+m_1^2\left(\frac{2}{7}-K_0\right)+\frac{15}{14}(g_y-2.00)\right]$$

with P, K_0 as the hyperfine interaction parameters and

$$m_z \approx m_1^2\beta_1^2 \qquad \Phi_x \approx \alpha_1^2\beta_3^2$$

$$m_x \approx m_1^2\beta_3^2 \qquad \Phi_y \approx \alpha_1^2\beta_2^2$$

$$m_y \approx m_1^2\beta_2^2$$

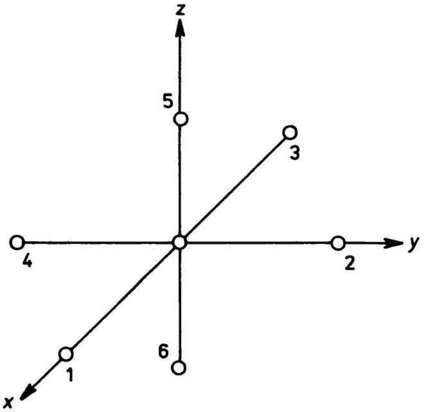


Fig. 10. Coordinate axes and numbering for the tetragonal d^1 system.

In the above expressions $\Delta E(A_g \rightarrow B_{1g})$, $\Delta E(A_g \rightarrow B_{2g})$, and $\Delta E(A_g \rightarrow B_{3g})$ are the corresponding electronic transitions from the ground state to the appropriate excited states.

Neglecting terms arising from the contribution of $d_{x^2-y^2}$ in the ground state d_{z^2} orbital, *i.e.* $m_1^2\beta_3^2$ and $m_1^2\beta_2^2$, in the expressions g_x and g_y, respectively, one can easily calculate that for a purely ionic case

$$\Delta E(A_g \rightarrow B_{2g}) \leq 19\,000\ \text{cm}^{-1}$$

$$\Delta E(A_g \rightarrow B_{3g}) \leq 19\,000\ \text{cm}^{-1}$$

Taking into account that only the absorption band at $\tilde{\nu} = 14\,000\ \text{cm}^{-1}$ may correspond to the $A_g \rightarrow B_{2g}$ or $A_g \rightarrow B_{3g}$ electronic transition one can easily calculate that $\Phi_x \approx \Phi_y \approx 0.74$ which is quite realistic and a strong indication of the significant amount of out-of-plane π and in-plane σ bonding.

Furthermore, it is probable that both σ and π bondings are similar in magnitude; one can easily calculate using $\Phi_x \approx \Phi_y \approx 0.74$ that

$$|\Delta E(A_g \rightarrow B_{2g}) - \Delta E(A_g \rightarrow B_{3g})| \approx 600\ \text{cm}^{-1}$$

which is in approximate good agreement with experiment (the absorption band at $\tilde{\nu} = 14\,000\ \text{cm}^{-1}$ has a definite extension towards high wavelength) [10—12].

On the basis of the simple CF theory one would predict

$$\Delta E(A_g \rightarrow B_{2g}) > \Delta E(A_g \rightarrow B_{1g})$$

or

$$\Delta E(A_g \rightarrow B_{3g}) > \Delta E(A_g \rightarrow B_{1g})$$

depending on the principal directions of the equatorial rhombic distortion.

Using the g_z expression and a value for g_z and assuming that $\Delta E(A_g \rightarrow B_{1g}) \approx 10\,000$ to $13\,000\ \text{cm}^{-1}$ one can calculate that $m_z \approx 0.05$.

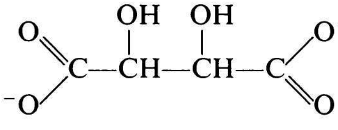
Assuming a moderate degree of covalency for the in-plane π bonding with $\beta_1^2 \approx 0.75$ to 0.85 one obtains $m_1^2 \approx 0.05$ to 0.06 or $m_1 \approx 0.22$ to 0.25.

Although rather approximate this estimate suggests a significant contribution of the $d_{x^2-y^2}$ orbital to the d_{z^2} ground state for a relatively modest equatorial rhombic distortion.

Structure of the $[\text{Ti}^{3+}]:[\text{NTA}] = 1:2$ *complex*

Even if one accepts that the experimental g-values are most consistent with an axially elongated field of $\mathbf{D}_{2h}$ symmetry in the complex, assignment of an exact structure to the Ti(NTA)_2 species remains a difficult task. However, with the available data, one can limit the possible structures and suggest a model for the chemistry involved.

First, recall that the nature of the anion (Cl^-, SO_4^{2-}) or the presence of massive amounts of TA ions



does not affect the pH 4 to 10 ESR or optical spectra. It seems reasonable to assume that only NTA or $\text{H}_2\text{O(OH)}^-$ are possible as ligands. Next, if we accept that the complex does not have the $\mathbf{D}_{3d}$ symmetry characteristic of uniformly tridentate NTA ligands, we can propose H_2O or OH^- as the axial ligand, *i.e.* the complex providing the signal at high pH is *trans*-$[\text{Ti(NTA)}_2\text{(OH)}_2]^{3-}$ or *trans*-$[\text{Ti(NTA)}_2\text{(OH)(H}_2\text{O)}]^{2-}$ (Fig. 8). These possibilities are consistent with a relatively small equatorial rhombic distortion ($g_y - g_x = 0.013$) but a sufficiently strong equatorial perturbation to provide the well-separated orbital singlet and requisite long spin-lattice relaxation time that are expected. Note $\Delta H_{\mathrm{p}\ \mathrm{p}}$ for the signal at room temperature is only (0.30 ± 0.05) mT.

Such a speculative assignment becomes more credible when we examine the critical pH region 2 to 3. Recall that Ti^{3+} ion hydrolysis has $K = 12.71$ at *ca.* 300 K and that $Ti(OH)_2^+$ is formed as the pH raised towards precipitation point (pH 3.5) [20—22]

$$Ti^{3+} + OH^- \leftrightarrows Ti(OH)^{2+}$$

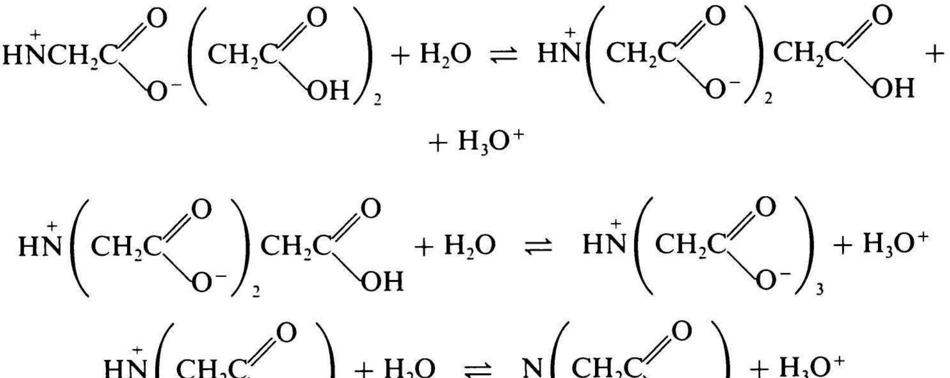
In the Ti(III)—NTA system, a second ESR signal appears at pH 3.0. It has similar linewidth to the first but is shifted to higher field ($\Delta g_0 = 0.0020 \pm 0.002$), and has much lower intensity. Significantly at pH 2.0 where it is the only species observed the frozen solution spectrum is qualitatively the same as at higher pH. We propose that a protonation of the principal complex has occurred, *i.e.*

$$[Ti(NTA)_2(OH)_2]^{3-} + H^+ \rightleftharpoons [Ti(NTA)_2(OH)(H_2O)]^{2-}$$

$$[Ti(NTA)_2(OH)(H_2O)]^{2-} + H^+ \rightleftharpoons [Ti(NTA)_2(H_2O)_2]^-$$

Protonation of the complexes bearing high net negative charge may occur at higher pH than the simple $Ti(OH)^{2+}$ or $Ti(OH)_2^+$ species.

The pK_a values for NTA ionization are 1.8, 2.5 and finally 10.6 for the zwitterion [10].



Further protonation of the coordinated NTA is clearly likely to occur, *e.g.*

$$[Ti(NTA)_2(H_2O)_2]^- + H^+ \rightleftharpoons [Ti(NTA)(NTAH)(H_2O)]$$

In this model such species will have reduced equatorial perturbation with the ground state degeneracy only slightly lifted so that the short spin-lattice relaxation renders their ESR signal undetectable.

It is obvious that as the pH drops further protonation equilibrium involving the NTA ligands becomes established leading to a region (pH 1.0 to 2.0) where only Ti(NTAH) exists as a dominant complex. The analysis of these equilibria lies beyond the ESR method. Careful titrimetric and stopped-flow kinetic analysis of the protonation sequence may provide a test of the model. No explanation has yet been found for the unchanging intensity of the band at $\tilde{\nu} = 14\,000\ \text{cm}^{-1}$ in the pH 2.0 to 3.0 region.

In conclusion, it is apparent that each ligand surveyed by *Fujiwara* and coworkers [10—12] requires a detailed study before trends in covalency in the series should be attempted from the ESR data. The complexity of the Ti(III)—NTA system led to the decision taken in this project to examine simple aqueous Ti(III) salts as a basis for future studies.

The complexity of these systems was particularly evident in the frozen solution spectra at pH 9.8. Even though continuous variation methods indicated nearly complete conversion to a $Ti(NTA)_2$ complex, additional resonances were observed. It was established that these additional resonances were not affected by altering the NTA concentration removing TA, changing to $Ti_2(SO_4)_3$, or adding Ti(IV) ions. Temperature cycling of the frozen solution in the interval 77 K to 230 K did not affect the spurious lines. However, they were power-saturated to a greater degree than the assigned peaks and tended to diminish at lower pH.

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